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Natural Resource Injury Report on Riparian Areas of the Bureau of Land Management within the Clark Fork River Basin, Montana

Based on reports prepared by

The University of Montana

and Montana State University

Under Cooperative Agreement 1200-99-007 through the
Rocky Mountain Cooperative Ecosystem Studies Unit (CESU)
Intermountain Region, National Park Service
Missoula, Montana

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Clark Fork River Operable Unit of the Milltown Reservoir Sediments NPL Site

PREFACE

This *Natural Resource Injury Report* characterizes the magnitude of injury from mining activities to natural resources held by the Bureau of Land Management (BLM) along the Upper Clark Fork River, Montana. Data from recent studies conducted on parcels of riparian lands held by the BLM were integrated with historical information of the area. Key foundation documents included the *Terrestrial Resources Injury Assessment Report, Upper Clark Fork River Basin* prepared for State of Montana Natural Resource Damage Litigation Program, the U. S. Environmental Protection Agency Ecological Risk Assessment, and several historical studies of the DOI lands.

Information from the following data reports constitutes the primary basis for the determination and quantification of injury as presented in this Natural Resource Injury Report:

- Gannon, J. E. and M. Rillig. 2002. *Relationship of Heavy Metals to Soil Respiration, Grant-Kohrs Ranch, and Bureau of Land Management Holdings, Montana*. University of Montana, Missoula.
- Kapustka, L. A. 2002. *Phytotoxicity Tests on Soils from the Grant-Kohrs Ranch National Historic Site, Deer Lodge, Montana.* **e**cological **p**lanning and **t**oxicology, inc., Corvallis, OR.
- Moore, J. N. and W. W. Woessner. 2001. *Geologic, Soil Water, and Groundwater Resources Report, Grant-Kohrs Ranch National Historic Site*. University of Montana, Missoula.
- Woessner, W. W. and M. M. Johnson. 2002. *Water Resource Characterization Report, 2000-2001*. Field Seasons at Grant-Kohrs Ranch National Historical Site. Technical Data Report submitted to the USDOI, NPS.
- Moore, J. N., B. Swanson, and C. Wheeler. 2001. *Geochemistry and Fluvial Geomorphology of Grant–Kohrs Ranch National Historic Site.* Department of Geology, University of Montana, Missoula, MT 59804-1296.
- Rice P. M. and J. Hardin. 2002. *Riparian Plant Community Structure at Grant-Kohrs Ranch*. Final Technical Data Report submitted to U.S. Department of Interior.
- Rice, P. M. 2002b. *Toxic Metals – pH Impact on Riparian Plant Community Structure at Grant-Kohrs Ranch*. Final Technical Data Report to U.S. Department of Interior.

Data were reviewed to assess quality and assign Quality Assurance levels by Dennis R. Neuman, director of the Resource Reclamation Unit, Montana State University, Bozeman. Almost all data were deemed "Enforcement Quality" as defined in the checklist procedures agreed to by ARCO and USEPA in 2000 for data generated at the Clark Fork River Superfund Sites.

The Record of Decision (ROD) for the Clark Fork River OU is scheduled to be issued by the USEPA in December 2002. Given the time frame for injury determination and natural resource damage claims development established under the under the Streamside Tailings Operable Unit Consent Decree (SSTOU CD, 19 April 1999), it was necessary to perform this assessment independent from, and without the foreknowledge of, the final remedy for the Clark Fork River Operable Unit. The USEPA states in its August 2002 Proposed Plan that it will select the 'no action alternative' for most of Reach B and all of Reach C of the CFROU. All 15 BLM parcels fall within these two reaches of the operable unit.

EXECUTIVE SUMMARY

This *Natural Resource Injury Report* documents the magnitude of injury from mining activities to natural resources of the Bureau of Land Management in the Clark Fork River Basin. This Report builds upon previous work conducted by the State of Montana in its Natural Resource Injury Assessment of areas within the Upper Clark Fork River Basin, but is predominantly based upon site characterization and natural resource damage assessment studies performed at Grant-Kohrs Ranch National Historic Site and BLM parcels along the Clark Fork River. Site-specific data reports for GRKO and BLM were released to the public and entered into the USEPA Administrative Record for the CFROU in July 2002. In particular, this assessment focuses on injury to soils of the riparian areas of the 15 land parcels administered by BLM.

The Constituents of Concern (CoC) emanating from past mining activities and from continuing upstream releases are arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn). Baseline concentrations were identified for As, Cd, Cu, Pb, and Zn from analyses of the soil profiles on the Grant-Kohrs Ranch National Historic Site (GRKO), a unit of the National Park Service that lies in Reach A of the CFROU. Measures of contamination revealed that:

- All surface soil samples in the GRKO floodplain had As, Cu, Pb, and Zn concentrations greater than 5-times the baseline value. Many samples outside the bounds of the floodplain (i.e., in historically irrigated fields, irrigation ditch sediments, and uplands) also showed elevated CoC concentrations.
- Copper concentrations in GRKO surface soils were up to 525-times the baseline.
- The total volume of GRKO soils with CoC >5-times baseline concentrations ranges from 293,000 m^3 (median depth) to 1,660,000 m^3 (maximum depth).

Of particular note, heterogeneous distribution of tailings occurs across the floodplain. This includes the presence of tailings buried under differing thickness of relatively uncontaminated soil. These hazardous substances in the soil are exchanged and transported in soil pore water and groundwater. Because moisture-deficit conditions are common in the region, especially in mid- to late summer, contaminants are frequently transported toward the soil surface.

Exposure to these hazardous substances results in direct toxicity to plants, loss of critical ecological functions mediated by microbes, loss of primary production, deviation of plant community composition from that expected for the area, and restricted development of root systems of plants. Site-specific studies demonstrated that:

- Growth and survival of herbaceous and woody species in controlled laboratory tests decreased as CoC (in particular pH-adjusted As, Cu, and Zn) levels increased.
- Root growth was among the most sensitive endpoints in all species tested.
- Aboveground herbaceous plant growth measured in field clip plots decreased as pH-adjusted As, Cu, and Zn levels increased.
- Patterns of plant cover on a small-scale (50 m^2 area) differed in relation to levels of CoC; known metal tolerant species were more prominent as pH-adjusted As, Cu, and Zn levels increased (e.g., tufted hairgrass, redtop bentgrass, and booth willow).
- Riparian plant community structure on a macro-scale (defined by recognizable breaks in species composition) deviated from expected baseline conditions in 63% of the GRKO riparian area.
- Patterns of soil respiration (a measure primarily of microbial activity) differed in relation to levels of CoC.
- Patterns of microbial community structure differed in relation to levels of CoC.

Episodic appearance of dead or dying vegetation results from the dynamic nature of physical transport mechanisms. The CoC are mobilized and reach elevated concentrations in the root zone of established

plant communities during drying periods. Suppression of root development also may contribute to the high rate of streambank failure noted along several reaches of the GRKO and BLM streamside.

Spatial heterogeneity (both vertical and horizontal) and the dynamic nature of the buried tailings preclude simple delineation of surficial deposits to define the extent of injury. Soil core, soil pit, and bank profile data indicated that surface soils generally had higher CoC concentrations than deeper soils. However, several samples demonstrated that lenses of highly contaminated soils occur below relatively uncontaminated surface soil; indeed the highest concentrations were observed in soil layers below the surface. Paired surface samples separated horizontally by five meters revealed that distributions of CoC were highly patchy.

As is the case at GRKO, hazardous substances from large-scale mining operations upstream of the BLM have contaminated the soils of these parcels. Soils on the BLM lands were elevated above baseline concentrations determined for the GRKO area. These baseline concentrations are considered representative of background concentrations basin-wide. The levels of contamination at BLM are significantly above background concentrations. Arsenic ranged from 1.4- to 17.1-times baseline; cadmium, from 1.0- to 11.4-times baseline; copper, from 6.7 to 102.5-times baseline; lead, from 2.0 to 17.5-times baseline; and zinc, from 3.5- to 83.9-times baseline. All 70 samples had Cu values >5-times baseline; 61 of 70 (87%) had Zn concentrations >5-times baseline; 36 of 70 (51%) samples had As >5-times baseline; 32 of 70 (46%) had Pb concentrations >5-times baseline; and 7 of 70 (10%) had Cd concentrations >5-times baseline. These effects diminish the capacity of the lands to supply the expected services of the localized areas of contamination in the floodplain. Statistical analysis of site-specific geochemical data from 10 of 15 BLM parcels provides a quantification of injury to natural resources on these parcels based on phytotoxic responses as defined in 43 CFR Part 11.

1 BACKGROUND INFORMATION

1.1 PHYSIOLOGY AND TOXICOLOGY OF METALS AND METALLOIDS

The five elements of concern in this case, As, Cd, Cu, Pb, and Zn, are naturally occurring trace elements. Copper and Zn are micronutrients required for plant, microbe, and animal growth and vigor. Arsenic, Cd, and Pb have no known physiological requirement. Because of the ubiquitous nature of these substances and their prominence in agriculture, a large body of literature has developed during the past century. Phytotoxicity endpoints reported in the literature include seed germination, root elongation, shoot mass and height, root mass and length, chlorosis, and seed production (yield). Microbial processes and soil invertebrate responses to these substances have also been studied extensively.

1.1.1 Essential vs. Non-essential Nutrients

Copper and Zn are required by living organisms for normal growth and survival. Copper is a constituent of a number of plant enzymes and activates certain enzyme systems, often influencing the photoreaction center within leaves and electron transport pathways in respiration in all cells. Similarly, in microbes and soil invertebrates, copper is also required for many enzyme functions. Copper is critical for proper functioning of electron transfer processes in respiratory cytochrome systems found in all living cells. Zinc is an important essential mineral for animal, microbe, and plant species. Zinc is a structural metal in many enzymes and is essential for enzyme activity. Zinc also contributes to the configuration of DNA and RNA. Plants and microbes must be exposed to levels of these elements in soil or water, and animals must have these elements in their diets in sufficient quantity to meet physiological needs. The exact required concentration varies with age, developmental stage, species, and in some cases in proportion to other essential elements. Organisms have evolved regulatory mechanisms that enable them to concentrate substances to levels above that in the environment at low environmental concentrations, or exclude substances at high environmental concentrations. For the essential elements, low bioavailable concentrations result in nutritional deficiencies. Homeostatic processes enable organisms to maintain fairly constant tissue concentrations across intermediate environmental concentrations, referred to as sufficiency levels. Excess levels of substances, that is above sufficiency levels, trigger toxicity. Arsenic, Cd, and Pb are not required for any organism.

1.1.2 Mechanisms of Toxicity

Toxicity of metals and metalloids is complicated by many physiological and environmental factors. Relationships of nutritional requirements, tolerance mechanisms, and factors affecting bioavailability influence susceptibility to these substances in soils. Nevertheless, metals and metalloids are known to cause a wide range of adverse effects in plants (Figure 1) and other organisms. These effects range from very specific physiological disorders to broader responses such as reduced growth or death. At the physiological level, metals and metalloids interfere with the plant's energy systems, enzyme functions, growth processes, and cell division. Death occurs at cellular, tissue, organ (e.g., leaves, stems, roots), and whole plant levels.

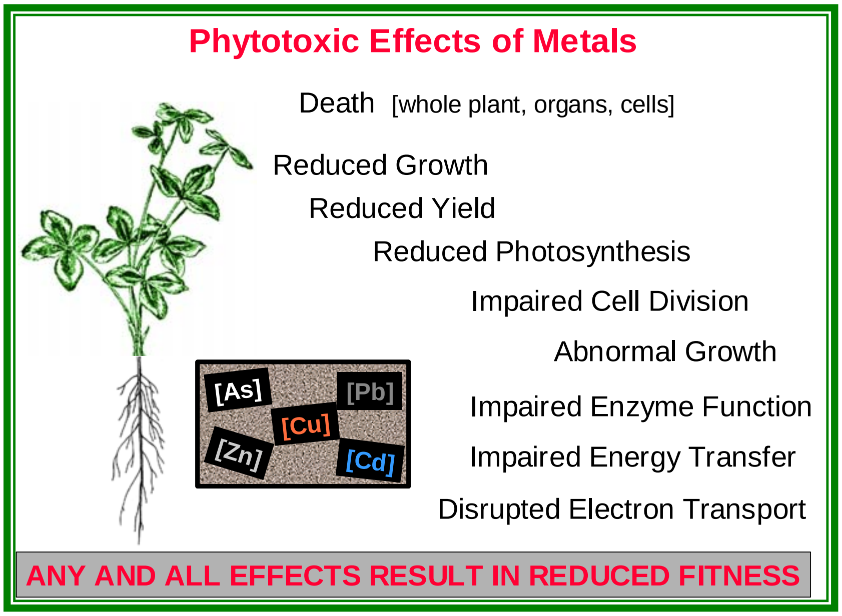

Figure 1. Phytotoxic effects of Constituents of Concern.

Toxicity occurs when an organism is overwhelmed by a chemical substance. In physiological terms, toxicity occurs when an organism loses the ability to maintain homeostasis, resulting in a loss of functions required for normal growth or to sustain life. Generally, this occurs at one or more internal cellular locations or may affect an entire organ. For plants, toxicity may also occur at the root surface without the substance ever entering the internal portions of the plant. Similarly, with microbes, toxic effects may occur at the external membrane surface. Extracellular enzyme function may also be diminished by metals and metalloids.

The site of toxic action may be an enzyme, a membrane, or a co-factor critical to some biochemical pathway. Often, there may be multiple sites of action for a particular substance and toxicity may be manifest in different ways, depending on how the primary modes of action and the cascade of secondary effects are linked. For many toxicity endpoints, such as reduced growth, reduced yield, or death, there are likely to be multiple disruptions of biochemical functions. For example, a phytotoxic response of reduced growth might be a result of impaired photosynthetic function, impaired respiration, and impaired water uptake by roots. Any one of these impairments would be detrimental over a longer time, but when all occur simultaneously, the response time is lessened.

1.1.2.1 Arsenic

Arsenic is a metalloid and, as such, displays chemical characteristics and behavior distinct from elements of the metal series (e.g., Cd, Cu, Zn and Pb). The availability of As to plants and the potential for plant toxicity depends on many factors, including soil pH, texture, fertility level, and plant species. In general, As is most available to plants in coarse-textured soils having little colloidal material and ion exchange capacity, and is least available in fine-textured soils high in clay, organic material, iron, calcium, and phosphate (NRCC, 1978). At comparatively low concentrations, As stimulates growth and development in various species of plants and animals. Such effects, referred to as *hormesis*, seem to be caused by over-compensation of regulatory hormones that modulate homeostasis. This results in non-linear responses to exposure.

Plants and other organisms tend to have a relatively poor capacity to discriminate arsenate from phosphate. Because phosphate is central to so many critical metabolic processes, As toxicity may be manifest with many endpoints. Inorganic arsenate of low solubility makes up the largest fraction of soil arsenic.

Arsenate is taken up by the phosphate carrier mechanism. Arsenic may link to sulfhydryl residues of protein, making the protein less than fully functional, thereby exhibiting toxic effects. Arsenic also inhibits fatty acid synthesis and degradation. It may also cause chlorosis (yellowing or bleaching of green plants). Phytotoxicity of arsenic in soils is reduced with increasing alkalinity, organic matter, iron, zinc, and phosphate levels (NRCC, 1978). Although As may be readily soluble and easily leached from soils, As toxicity can persist in soil for several years (Woolson, 1975). An early indication of plant injury by sodium arsenite is wilting caused by rapid loss of turgor (the normal distension in a live cell), whereas stress caused by sodium arsenate does not involve rapid loss of turgor (NAS, 1977). Arsenite acts primarily by inhibiting light activation, probably through interference with the pentose phosphate pathway (Marques and Anderson, 1986). Phytotoxicity of organoarsenical herbicides is characterized by chlorosis, cessation of growth, gradual browning, dehydration, and death (NAS, 1977). Although As is not an essential plant nutrient, small yield increases have been observed at low soil As levels, especially for more tolerant crops such as potatoes, corn, rye, and wheat (Woolson, 1975), consistent with the phenomenon of hormesis. However, for most crop plants, significant depressions in yields are evident at 25 to 85 ppm of total soil As (NRCC, 1978). A soil concentration as low as 2 ppm soluble As is considered the threshold level for marked damage to alfalfa and barley, whereas 3.4 to 9.5 ppm soluble As causes "poor condition" of young seedlings (Chapman, 1966). Phytotoxicity in Bermuda grass ranged from 45 to 90 ppm in sand and clay soils, respectively. Alfalfa grew poorly in soils containing only 3.4 to 9.5 ppm when soils were acidic, lightly textured, low in phosphorus and aluminum, high in iron and calcium, or with excess moisture (Woolson, 1975).

1.1.2.2 Cadmium

Cadmium (Cd) is not essential to any living organism, and is a known teratogen, carcinogen, and mutagen in animals (Eisler, 1985). Many interactive factors modify the plant uptake process. Cadmium uptake is influenced by the sulfides and sulfites present in the soil. Also, associated with ammonium uptake, the plant releases protons into the soil to balance the electrical charge associated with the uptake of ammonium. This causes the pH in the immediate vicinity of the plant root to drop. In turn, this causes more Cd to be released from soil particles and become available for uptake by the plants. Cadmium usually remains in the upper portion of the soil profile. Calcium, Zn, and H ions can compete with Cd for sorption sites in soil or can significantly desorb Cd from soil. Cadmium availability depends on adsorption/desorption rates, pH, Eh, and chemical speciation. Plant- or fungi-mediated uptake of Cd occurs as the divalent cation (Cd^{+2}). Cadmium is taken up by roots and translocated sparingly in various forms of organic and inorganic molecules throughout most plant tissues.

Cadmium interferes with calcium, a substance that is pivotal to many regulatory processes in cells. Cadmium reduces photosynthesis, growth, and yield. Additive phytotoxic effects occur with zinc and cadmium. Cadmium and Zn are closely associated in geologic deposits and have a similar chemical behavior. The Cd to Zn ratio in soils is thought to be biologically important, as Zn may lessen the toxic effects of Cd, and Cd may displace Zn, creating a potential deficiency. Cadmium phytotoxicity has been reported using a variety of endpoints including photosynthesis, growth, yield, and morphological aberrations. Growth inhibition and morphological deformation were apparent in lettuce and soybeans at soil Cd concentrations between 4 to 14 ppm. At these same concentrations, Cd affected tomatoes and cabbage less than it affected lettuce and soybeans. At a higher concentration (i.e., 150 ppm soil), Cd affected photosynthesis, although its mode of action on this process is unknown. Additive phytotoxic effects of Zn and Cd were found using split root tomato plants (Smith and Brennen,1983). The uptake of the two metals was not affected, although other plant physiological processes were altered through the interactive effects of the two metals.

1.1.2.3 Copper

Copper phytotoxicity is expressed in many ways: reduced growth, reduced branching, thickening, and abnormally dark coloration in the rootlets, chlorosis, and reduced yield. Excess Cu inhibits a large number of plant enzymes and interferes with photosynthesis, pigment synthesis, respiration, and membrane integrity. As is the case with Cd or Zn, Cu is a transition metal.

Threshold response concentrations and endpoints affected vary among species tested. Copper generally has greater effect on plant root growth than shoot growth (Baszynski *et al.*, 1982; Gupta and Mukherji, 1977). Root elongation is a more sensitive indicator of Cu effects than root initiation (Hogan and Rauser, 1981). Tomato growth was inhibited at soil Cu concentrations above 150 ppm at pH below 6.5 and above 330 ppm at pH above 6.5 (Rhoads *et al.*, 1989). Black bindweed (*Polygonum convolvulus* L.) had reduced survival at soil Cu concentrations of 125 ppm and reduced seed production at 200 ppm (Kjær and Elmegaard, 1996). Chhibba *et al.* (1994) found that wheat yield significantly decreased with soil Cu concentrations greater than 40 ppm with a calculated threshold concentration of 8 ppm Cu. Oats (*Avena sativa*) exposed to 400, 600, and 800 ppm Cu on cultivated soils and 150 and 300 ppm Cu on uncultivated soils had reduced grain and straw yields for both soils at the lowest concentration tested one and four years after application (Tikhomirov *et al.*, 1988). Plants were more sensitive to Cu additions in uncultivated soil. Oat yields were significantly reduced with 100 ppm Cu and higher in soil (Rhoads *et al.*, 1992), but at a Cu concentration of 400 ppm, yields were improved by the addition of lime and phosphorus. Mosses and lichens vary greatly in their sensitivity to Cu, with threshold concentrations (for survival) of Cu in soil ranging between 80 and 1000 ppm (Folkeson and Andersson-Bringmark, 1988).

Plant species vary greatly in their genetic potential for tolerating elevated Cu concentrations. Cu tolerance can evolve rapidly in populations of many short-lived plant species through the natural selection of those few tolerant individual plants present in normal populations on uncontaminated soils (Wu and Bradshaw 1972, Turner 1994). Trees and other long-lived species show little evidence of Cu tolerance. Although mature trees may survive at Cu contaminated sites, regeneration through seedlings (the most sensitive life stage) appears to be inhibited. The result is that sites heavily contaminated with Cu alone, or Cu with other metals, often support a sparse flora with low species richness (Ernst, 1990).

Copper is toxic to many species of fungi. Fungal species diversity decreased with increasing Cu concentration during a five-month laboratory study; 31, 31, 30, 27, 25, and 19 fungal species were isolated from soils containing 0, 100, 200, 400, 800, and 1600 ppm Cu, respectively (Yamamoto *et al.*, 1985). Decreases in soil fungal diversity related to heavy metals have been reported in other studies (Lawrey, 1977; Zibilske and Wagner, 1982). In soils containing populations of fungi, bacteria, and actinomycetes, Cu had the greatest impact on fungi (Wang *et al., 19*86).

Copper and other heavy metals generally are known to inhibit decomposition of soil organic matter, soil respiration, nitrogen mineralization, and nitrification in a manner dependent upon the form of the chemical, the amount of organic matter in the soil, and the soil pH (Hattori, 1992). In response to Cu, microbial species diversity is lowered and microbial functions are impaired. Microbial biomass carbon and phosphorus, substrate-induced respiration, and denitrification decreased significantly with increasing metal contamination in the soil in a pasture contaminated with a timber preservative containing Cu, Cr, and As (Bardgett *et al*., 1994). Metal stress caused a decrease the degradative capabilities of soil bacterial communities in metal contaminated and uncontaminated soil from Canada and Germany (Burkhardt *et al*., 1993).

Biological nitrogen fixation by heterotrophic nitrogen-fixing bacteria was reduced significantly at soil pH >6 and 50 ppm Cu in soil (Mårtensson, 1993). At 125 ppm soil Cu, nitrogen fixation by surface-dwelling cyanobacteria was significantly reduced. Heterotrophic biological nitrogen fixation was significantly reduced at soil Cu concentrations of 75 ppm, independent of soil pH or carbon and nitrogen content of soils (Mårtensson, 1993) even though nodulation is not affected at such low concentrations. Nodulation of clover was detected in soils up to 370 ppm Cu (Smith, 1997).

The effects of Cu on plant communities are a function of direct toxicity to individual plant survival and reproduction, alterations of soil-mycorrhizal-plant interfaces, and disruption of plant decomposition processes that release nutrients to the soil. Several studies document the reduction in plant community diversity and productivity resulting from exposure to Cu and other heavy metals. For example, the plant community at the refinery site in Merceyside, northwest England with mean soil Cu concentrations of 11,000 ppm was low in diversity and dominated by metal-tolerant species, such as *Agrostis stolonifera* and *Festuca rubra* (redtop bentgrass and red fescue; Hunter *et al*., 1987). In these species, the binding of Cu to root cell walls reduced the effects of increases in the soil Cu concentrations. Although the water-soluble

Cu concentration was 55 times greater at the refinery than at the control site, there was only a four-fold increase in the leaf and shoot concentration in *A. stolonifera*. Copper concentrations in plants at the refinery site also varied with the season. The highest concentrations in *A. stolonifera* occurred during winter months due to translocation of Cu into older shoots and leaves prior to senescence and due to surface deposition of particulates. Copper concentrations in plants were diluted by new growth in the spring.

Litter decomposition rates were nearly seven-fold higher at a control site compared to a site 1 km from a Zn smelter in Pennsylvania (Cu concentration of 340 ppm in soil), indicating that not only the structure, but also the biological functioning of the soil community was disrupted (Strojan, 1978). A significant reduction in leaf litter decomposition rate near the smelter could lead to an increase in the standing mass of un-decayed litter, eventually affecting primary productivity by limiting the cycling of essential plant nutrients (Tyler, 1972). Aerially deposited metals concentrate in the upper organic horizons by ion exchange, surface adsorption, and chelation-reaction mechanisms and persist for long periods of time, hindering recovery of the soil community.

Grassland species composition changed with the accumulation of 280 to 327 ppm Cu in the top 5 cm of soil from a facility emitting Cu primarily aerially as Cu oxides, (Lepp *et al*., 1997). The area was sown with known grass mixtures in 1975, and plant community composition was determined approximately 20 years later. The species compositional structure and aerial coverage changed significantly from the composition of the original seed mixture. Perennial ryegrass (*Lolium perenne*) was absent from most current plant communities, even though seed mixtures contained 20% to 25% ryegrass. *Agrostis capillaris* showed the greatest tolerance of Cu and was the dominant grass at all sites (*A. capillarus* from uncontaminated sites did not possess the same degree of Cu tolerance, Dueck *et al*., 1987). Broad-leaved herbs were found to be very sensitive to a combination of elevated levels of Cu.

Elevated Cu concentrations also may affect plants indirectly through effects to fungi. Endophytic fungi enhance resistance of their host plants to insect herbivores, but some species are very sensitive to Cu and other heavy metals. Conversely, metals may affect endophytic fungi indirectly by altering environmental factors such as stand density, site humidity, and tree height (Ranta *et al*., 1994). The mycorrhizal association between higher plants and ectomycorrhizal fungi can modify the toxicity of heavy metals for higher plants. However, highly contaminated sites are directly toxic to mycorrhizal fungi, limiting colonization to a small set of non-mycorrhizal, Cu-tolerant species (Griffioen *et al*., 1994).

1.1.2.4 Lead

Lead, a member of the metal group on the periodic table, is tightly held in the soil and is taken up sparingly by plants at low pH, low phosphate, and low soil organic matter. Soils with higher organic content and similar pH will hold Pb and other heavy metals more strongly so that a smaller percentage of Pb is made available to plants. Interactions between Pb, other elements, and environmental factors complicate the process of establishing toxic soil Pb concentrations.

Toxicosis from Pb in plants is expressed by reduction in growth, photosynthesis, mitosis, and water absorption. Roots in contact with Pb degenerate as cell division in root meristems decreases (Wierzbicka, 1989). The activity of many enzymes is inhibited as Pb blocks sulfhydryl groups in proteins (Eisler, 1988). Lead in roots probably competes with calcium, which plays a role in cell division of actively growing roots. Thus, lead causes generalized disruption of cell division, impairing root growth and function. Lead does not affect mature leaf tissues as readily as growing leaf tissues, where inhibition of chlorophyll and carotenoid synthesis may be an indirect effect of root inhibition. Lead inhibits plant respiration and photosynthesis through disturbance of electron transfer reactions and $C0_2$ formation in chloroplasts (Miles *et al.*, 1972). Phytotoxic Pb levels in soil range from 100 ppm to 2,000 ppm. Sensitive crops may be considerably damaged in soils with higher available Pb content (i.e., lower pH) at levels lower than 1,000 ppm. At 1,000 ppm total soil Pb level, significant yield reductions may occur in alfalfa, barley, oats, and lettuce in soils with pH values less than 6.0.

1.1.2.5 Zinc

Zinc is an important essential mineral for most animal and plant species. Zinc is a structural metal in many enzymes and is essential for enzyme activity (Riordan and Vallee, 1976). Zinc also contributes to the configuration of DNA and RNA (Kabata-Pendias and Pendias, 1992).

Plant and fungal-mediated uptake of Zn is influenced by soil pH, soil composition, organic matter, and phosphorus levels. Zinc availability to plants is enhanced in acidic soils, as with many metals. High levels of soil calcium and phosphorus reduce Zn availability to plants, lowering the risk of plant toxicity (Kabata-Pendias and Pendias, 1992). Plant uptake of Zn is also influenced by the organic matter content of soil, chelating compounds, and soil fertility (Kabata-Pendias and Pendias, 1992).

Symptoms of Zn toxicity include stunted growth, reduced yields, reduced leaf size, necrosis of leaf tips and shoot apices, a reddish tint near the basal part of leaves, and curled, distorted foliage. Total soil Zn concentrations in excess of 600 ppm in soil were associated with yield reductions greater than 25 percent in many crop species. Typical phytotoxic criteria for total soil Zn range from 250 to 500 ppm (Kitagishi and Yamane, 1981; Chapman, 1966). Yield reductions in most species are low at concentrations less than 200 ppm, while levels greater than 200 ppm result in increasing yield reductions for many crops. Vegetative yields for barley and wheat were reported to decrease by 16% and 18% at total soil Zn concentrations of 200 ppm and 300 ppm respectively (Boawn and Rasmussen, 1971). Mitchell *et al*. (1978) noted reductions in wheat grain yields of 3 to 14% in the 100 to 180 ppm total soil Zn range and 12 to 29 percent at 340 ppm total soil Zn (CH2M Hill, 1986). A wide range of Zn phytotoxic levels has been reported for plants. Phytotoxic Zn levels range from 60 ppm for wheat plants (Takar and Mann, 1978) to more than 800 ppm for swiss chard (Boawn, 1971). Most values for cereal grains and forages fall between 189 ppm and 560 ppm, with 35 and 20 percent yield reductions, respectively (Mitchell *et al*., 1978; Boawn and Rasmussen, 1971). Boawn and Rasmussen (1971) reported 20 percent yield reductions for barley, wheat, and alfalfa at plant tissue levels of 540 ppm, 560 ppm, and 295 ppm, respectively. Zinc phytotoxicity to barley seedlings was reported in the range of 160 ppm to 320 ppm (Davis *et al*., 1978).

1.1.3 Toxicity Threshold Values

Toxicity thresholds refer to concentrations above which organisms exhibit adverse effects such as reduced growth or increased mortality. Data from a single experiment or from several studies (either laboratory or field observations) are used to identify thresholds (Figure 2). Literature reviews of toxicity studies are often aimed at identifying the lowest concentration of a substance at which adverse effects were reported. These values are useful in attempting to find an environmental concentration protective of all species. However, many soil factors alter the concentration response relationships. Most commonly, pH, organic matter content, soil texture, and relative amounts of other substances (e.g., calcium, iron, etc.) influence bioavailability and therefore the threshold concentration for a particular field situation. Also, the chemical form of the substance can be very significant. Because of this, some literature reviews have emphasized ranges of toxicity threshold concentrations. Comparisons of data reporting the most sensitive species response to those that are most resistant help to define expectations under field situations. As environmental concentrations approach the higher threshold values, it becomes more likely that many more species would be harmed (FigFigure 2). At environmental concentrations substantially above the higher threshold values, serious and sustained injury to most or even all species can be expected (Figure 3). Ranges of soil concentrations (ppm or mg/kg) as general indications of phytotoxicity may be compiled from several independent reviews and studies (Table 1).

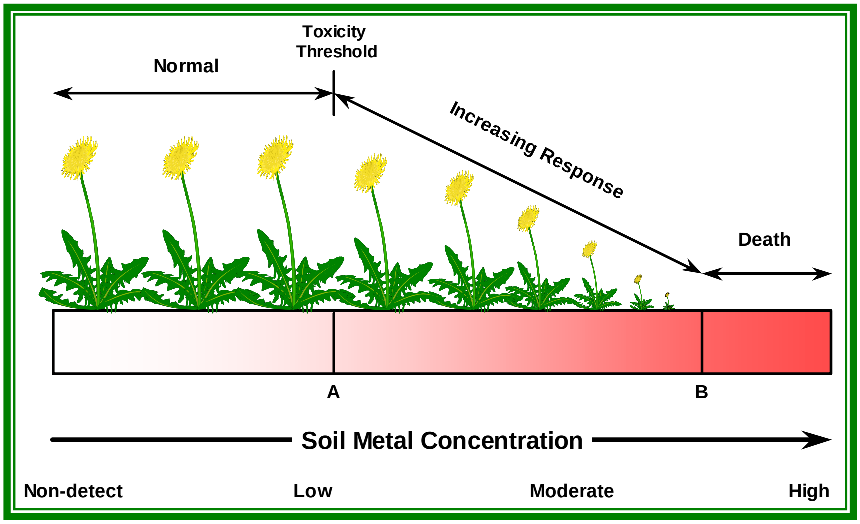

Figure 2. Relationship of CoC concentration and phytotoxic response.

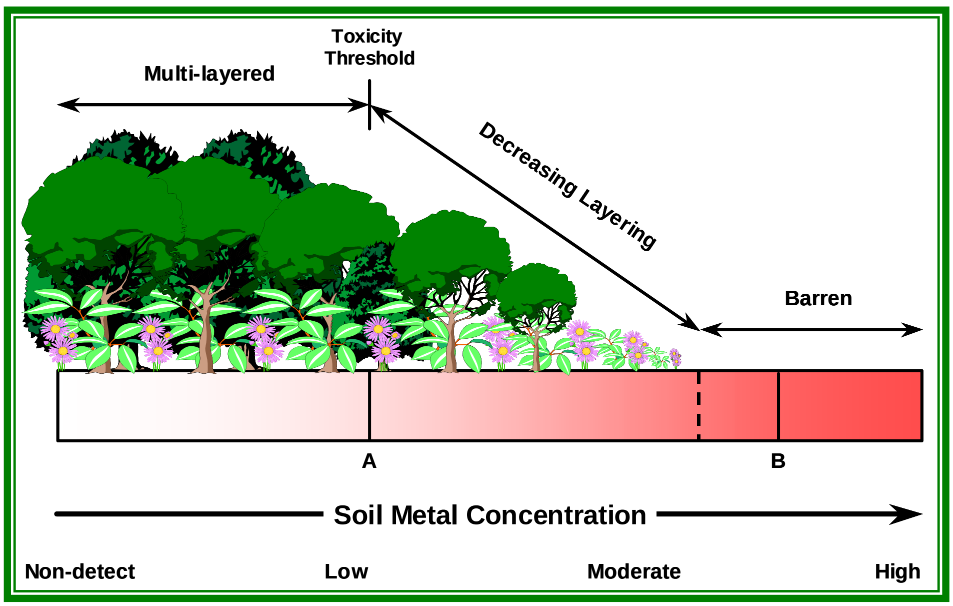

Figure 3. Relationship of metal concentration and vegetation response.

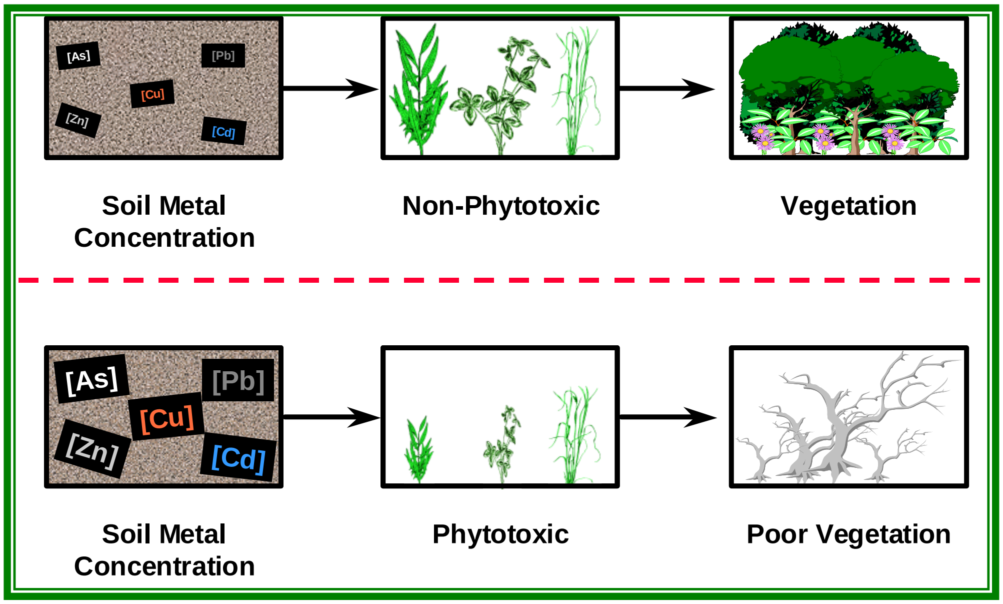

Figure 4. Relationship of phytotoxicity and vegetation response.

The type and degree of response depends on the concentration of the metal or metalloid to which the plant is exposed. For each metal or metalloid, a plant will have a toxicity threshold concentration. That is, at lesser concentrations normal physiological activities will occur. The degree of response increases with increasing concentration of the substance. At some concentration, the poisoning effect is such that death of the plant occurs (Figure 4).

Table 1.	**Phytotoxicity Threshold Values.**		
element	**low threshold[1]**	**upper threshold[2]**	**Draft EPA Eco-SSLs[3]**
As	10	100	36
Cd	3	100	20
Cu	60	150 (250)	95
Pb	100	1,000 (10,000)[4]	148
Zn	70	400	132

[1] Lowest reported value from various sources (including Alloway, 1995; **ep** and **t**,1995; Kabata-Pendias and Pendias, 1992).

[2] Highest reported value from various sources (including Alloway, 1995; **ep** and **t**,1995; Kabata-Pendias and Pendias, 1992).

[3] Draft concentrations from US EPA Ecological Soil Screening Levels to be published in 2002. Values are intended to be a safe level for soils with maximum bioavailability.

[4] **ep** and **t**,1997.

Similar ranges exist for soil microbes and soil invertebrates, though microbes tend to have lower low thresholds and slightly higher tolerance levels than other groups. Metals and metalloids interfere with membrane function, biochemical pathways, electron transport processes of soil microorganisms and soil invertebrates (Figure 5).

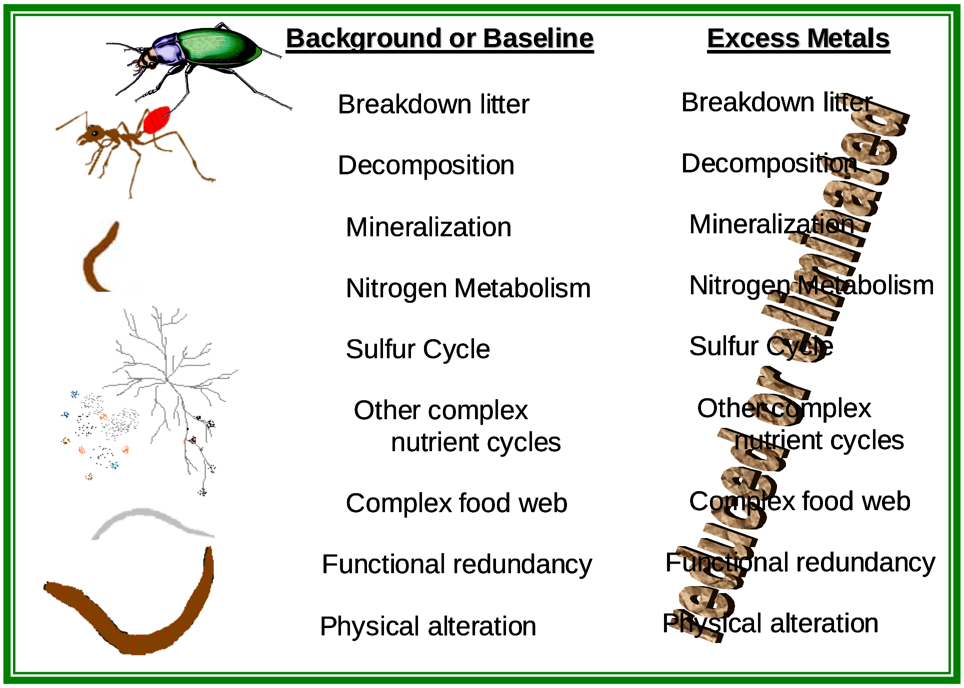

Figure 5. Relationship of CoC concentration toxicity to microorganisms and soil invertebrates.

1.1.4 Ecological Consequences of Toxicity

Toxicity test methods are designed to measure the response of individuals to test substances or mixtures of test substances. Except for rare or endangered species, public policy and law are focused on population effects or higher levels of ecological organization (e.g. community or system's functions).
At soil metal concentrations above the deficiency zone but below the phytotoxic threshold concentrations, the soil is not toxic and, therefore, normal, complex communities will develop. At concentrations above the threshold, the soils are phytotoxic. This results in poor or no vegetation. In a plant community, there are many individuals of many species. Typically, there are several canopy layers formed by the different species. For example, an upper canopy of mature trees, one or more sub-canopy layers formed by smaller trees or shrubs, herbaceous layers, and ground layers. As toxicity effects occur in different species, the complexity of the community decreases. Where conditions become toxic to most species, the landscape becomes barren. Because field conditions include many other stresses such as drought, temperature extremes, disease, and insect infestations, the landscape can become barren at concentrations less than might be required to kill plants in short-term laboratory tests.

Bacteria and fungi are part of every ecological system. In the terrestrial environment, decomposition of organic material governs the rate of mineralization (release of essential nutrients from organic form to inorganic ions). This, along with microbial processes that alter the oxidation state of various anions and cations, is an important determinant of soil fertility. Direct interactions with plant roots in the form of associative bacteria and symbiotic bacteria and mycorrhizal fungi have been shown to have critical roles in governing diversity and productivity of plant communities. Mycorrhizal fungi are important for development of dynamic plant communities. Estimates are that more than 95% of all plant species and 99% of all plant individuals are mycorrhizal dependent – that is to say that elimination of mycorrhizal associations leads to dramatic shifts in the composition of the plant community. Similarly, associative and symbiotic soil bacteria are critical to the normal functioning in the rhizosphere, a zone around the roots of plants.

Soil invertebrates have substantial influence on development and maintenance of fertile soils. Various nematodes, earthworms, centipedes, springtails, enchitrids, isopods, spiders, and insects live in soils. Interactions of microorganisms and soil invertebrates result in the breakdown of plant roots and litter. Soil invertebrates not only accelerate decomposition of plant litter, they also influence soil structure and aeration as they burrow, ingest, digest, transform, and defecate in the upper horizons of soil. These conversions provide turnover of nutrients in soil that are critical to soil fertility.

Toxicity to microorganisms and soil invertebrates can have severe consequences affecting ecological systems (Figure 6). The biomass of microorganisms and soil invertebrates exceeds the mass of vertebrates. At modest concentrations of hazardous substances, species changes occur among the microorganisms and to some extent soil invertebrate communities. Often, such changes do not markedly alter ecological functions. However, with sustained exposure to high concentrations of hazardous substances, ecological services provided by microorganisms and soil invertebrates are diminished. The consequences of such sustained injuries are extended to the plant community.

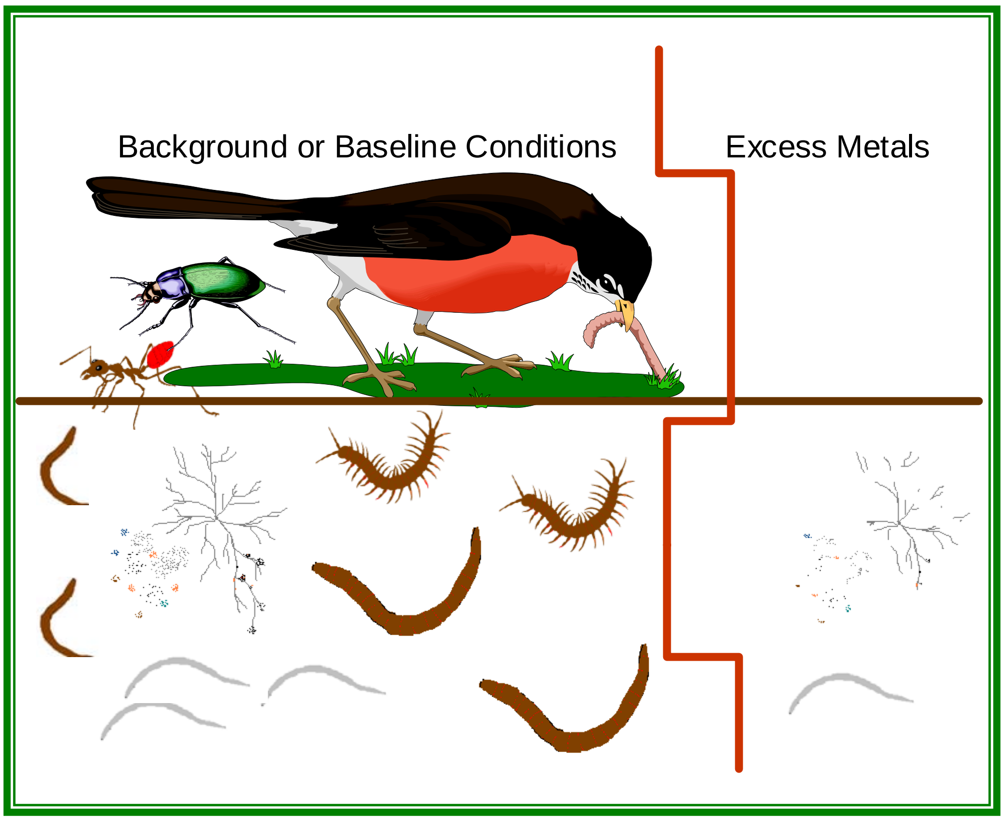

Figure 6. Consequence of toxicity to microorganisms and soil invertebrates.

2 GEOLOGIC RESOURCES – BLM RIPARIAN SOILS

2.1 DESCRIPTION OF THE RESOURCE

The BLM manages 15 parcels within the Clark Fork River floodplain (Figure 7) comprising a total area of approximately 974.5 ha (2,409 ac), of which 192.2 ha (475 ac) are riparian lands. These land parcels lie within Reaches B and C of the CFROU, approximately 70 km (43 highway miles) along the Clark Fork River. Site data were obtained from ten of the 15 parcels. These ten parcels were selected for sampling because of the prominence of the floodplain related to these particular tracts.

BLM land management is guided by the Federal Land Policy and Management Act (FLPMA) of 1976. This Act directs BLM to use "multiple use management," defined as

> '…management of the public lands and their various resource values so that they are utilized in the combination that will best meet the present and future needs of the American people.' FLPMA [43 U.S.C. 1702] Sec 103(c)

Specifically, FLPMA dictates, in part, that:

> '…the public lands be managed in a manner that will protect the quality of scientific, scenic, historical, ecological, environmental, air and atmospheric, water resources, and archeological values…will preserve and protect certain public lands in their natural condition…will provide food and habitat for fish and wildlife and domestic animals; and that will provide for outdoor recreation…' [FLPMA, [43 U.S.C. 1702] Sec. 102(a)(8)]

The BLM tracts in this study are managed for the multiple purposes of wildlife habitat, livestock grazing, and recreation. The degree to which one purpose is emphasized over another varies from parcel to parcel.

2.2 INJURY DEFINITIONS

Soil injury is defined in 43 C.F.R. § 11.62 (e). According to this regulation, injury to geological resources has occurred if a release or threatened release of hazardous substances causes, or has the potential to cause, any of the following:

- pH<4.0 or >8.5;
- salt saturation yielding a salt saturation value >2 millimhos per centimeter in soil;
- decreased water holding capacity such that plant, microbial, or invertebrate populations are affected;
- impedance of soil microbial respiration to an extent that plant and microbial growth have been inhibited;
- inhibition of carbon mineralization resulting from a reduction in soil microbial populations;
- toxic response to soil invertebrates; or
- phytotoxic response, such as retardation of plant growth.

A condition satisfying any one of these definitions is sufficient to establish injury to the resource.

2.3 INJURY DETERMINATION AND QUANTIFICATION

Injury was based on historical information and more recent data gathered specifically to quantify injury to soils on the DOI lands. Recent data on riparian and upland soils are presented in six data reports (Gannon, 2002; Kapustka, 2002; Moore, 2000; Moore and Woessner, 2001; Moore *et al.*, 2001; and Woessner and Johnson, 2002). The quality of data was evaluated and found to be of sufficient quality for their intended uses (Neuman, 2001, 2002). Nearly all of the soil, sediment, and water CoC data were found to meet the highest standards (i.e., enforcement quality as defined in the checklist procedures agreed to by ARCO and USEPA in 2000 for data generated at the Clark Fork River Superfund Sites).

2.3.1 Baseline Metals Conditions

Baseline concentrations of CoC represent the natural levels of these substances prior to mining activities. Previous reports as well as analyses of new data were considered in establishing baseline concentrations for each CoC. The information for this section was derived from the technical report by Moore and Woessner (2001). Data on soil CoC baseline concentrations were obtained from deep soil cores collected on the GRKO in 2000. These data were compared to values reported from previous efforts to determine CoC baseline concentrations.

2.3.1.1 Baseline Sampling Design

Soil profile sampling was focused on areas along the Clark Fork River floodplain and on the Clark Fork River channel cut banks on GRKO. Two hundred and seventy-three subsurface soil samples to depths of approximately 120 cm were collected from 39 locations (Moore and Woessner, 2001). This was comprised of 15 streambank samples, 3 pits, and 21 cores taken with a "Geoprobe." Chemical analyses were performed using standardized processing and measurement methods. Samples were digested according to a modified EPA Method 3050B for the extraction of total metals. Digests were analyzed for total metals by ICAP-ES as per EPA Method 200.7. Analytes included aluminum (Al), As, calcium (Ca), Cd, chromium (Cr), Cu, iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), phosphorus (P), Pb, and Zn.

2.3.2 BLM Geochemical Sampling Design and Locations

The sampling of BLM lands was designed to characterize the extent of contamination of soils near the current or previous channels of the Clark Fork River and therefore likely to have received deposits of mining/milling wastes from the Butte/Anaconda area (see Moore 2000; Figure 7, Figure 8, Figure 9). The number of sampling locations per site varied from 2 to 21. Due to these differences in sampling intensity and the expected differences in levels of CoC among the Tracts, it may be best to consider each tract as a separate entity rather than group all into a single analysis. Here we present summaries of all tracts as well as for individual tracts.

Baseline concentrations of the CoC established for the GRKO were applied to the BLM parcels for comparisons of the magnitude of contamination. These values are the most comprehensive data for the pre-mining period for the Clark Fork River.

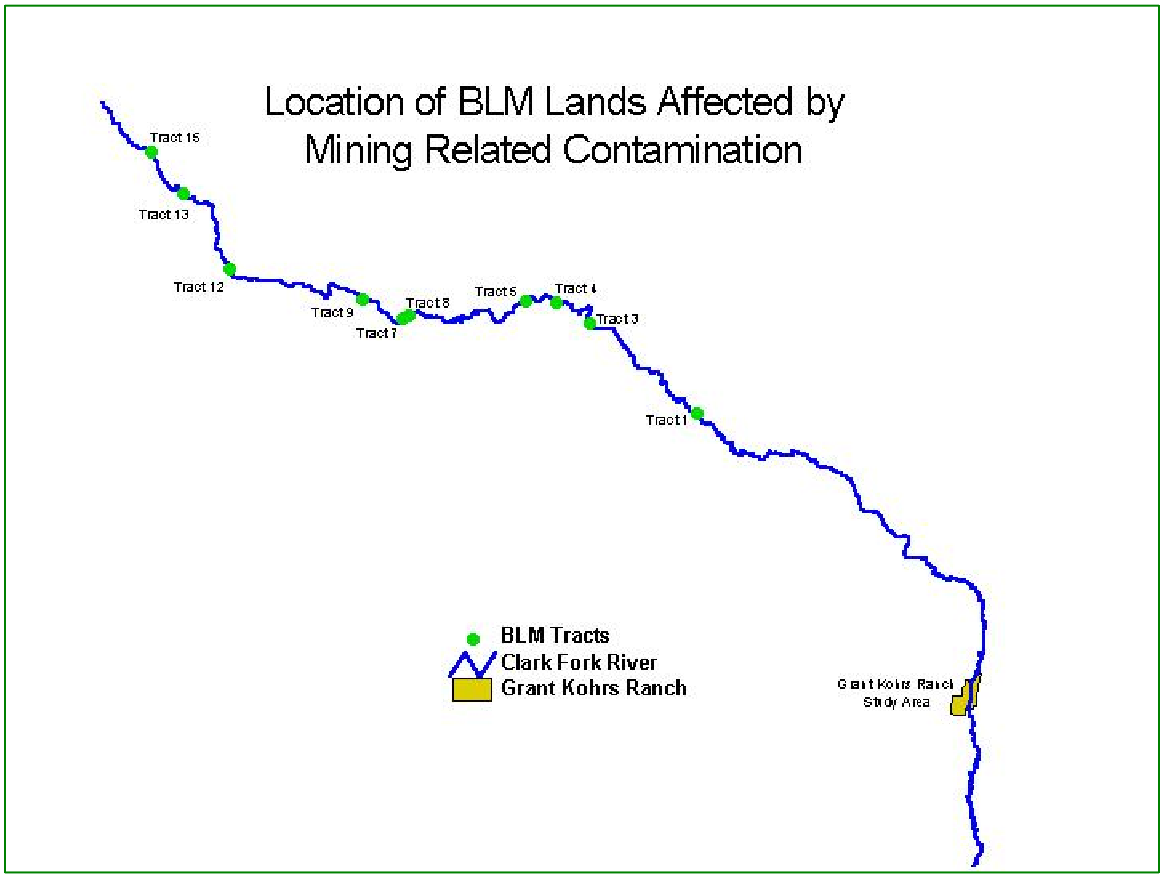

Figure 7. BLM tracts in CFROU Reach B and C.

2.3.3 Historic Phytotoxicity Tests

Several prior phytotoxicity studies have been performed on slickens in the CFROU. These include studies conducted for the RI/FS (Montana State University *et al*., 1989a), the State of Montana Injury Assessment (Lipton, *et al*., 1993), and an academic study (Rader *et al.*, 1997).

The Streambank Tailings and Revegetation Study (STARS), a component of the Silver Bow Creek RI/FS, was initiated to develop remedies for *in situ* treatment of tailings deposited along Silver Bow Creek (Montana State University *et al*., 1989a). Greenhouse phytotoxicity tests were performed on six slickens soil samples. The test species were selected for their tolerance to acidic soils with high metal concentrations. The authors noted that no native plants had evolved tolerance mechanisms to cope with the conditions found on slickens, thus no native species were included in the tests. Nevertheless, even the tolerant species used in their tests had 100% failure (i.e., all plants in all trials either failed to germinate or died shortly after emergence).

Four slickens samples were evaluated for phytotoxic responses for the State of Montana Injury Assessment (LeJeune, *et al.*, 1996; Lipton, *et al*., 1993). Alfalfa, lettuce, wheat, and hybrid poplar were used as test species. In two of the samples, germination and emergence of the herbaceous species was completely inhibited; in one sample emergence ranged from 0- to 25% for the three species; and in the fourth sample emergence ranged from 5- to 75%. Of those seedlings that survived, growth was significantly less than controls for alfalfa and lettuce in all samples, and was significantly less than controls in three of the four samples for wheat. Mortality of hybrid poplar was 100% in three of the four samples and was 40% in the fourth sample. Growth of shoots and roots in the fourth sample was inhibited by approximately 75% compared to controls. All four samples were classified as severely phytotoxic.

Rader *et al*. (1997) tested slickens soils from the GRKO at various dilutions (made with uncontaminated soil) using barnyard grass (*Echinochloa crusgalli*), lettuce (*Lactuca sativa*), radish (*Raphanus sativus*), and redtop bentgrass (*Agrostis gigantea*). They found that root growth was the most sensitive endpoint. In 100% slickens material, all four species, even the generally metals tolerant redtop bentgrass, were inhibited. Barnyard grass had limited emergence in treatments having 75% and 50% slickens with the remaining portion of the test soil made up with uncontaminated soil. Lettuce has a very low level of emergence at the 25% slickens level. Radish and redtop bentgrass emergence occurred only at slickens concentrations of 12.5% and less. Comparing root growth of emerging plants, barnyard grass was the most sensitive species.

2.4 FINDINGS

Seventy surface soil samples (upper 30 cm in 2000 upper 15 cm in 2001) were analyzed for CoC. Comparison of the 30 cm and 15 cm soils samples showed no statistical difference in CoC concentrations, permitting the 2000 and 2001 data to be pooled. Concentrations were generally lower from BLM parcels than upstream on the GRKO (Table 2, Table 3). Tracts 1, 5, and 9 had the highest concentrations of Cu and Zn. BLM levels were consistently above baseline including a maximum Cu concentration of 102.4 times the baseline. Zinc reached a maximum of 83.9 times the baseline. Mean values ranged from 3.2 times the baseline for Cd to 35.0 times the baseline for Cu.

Table 2. Multiples of CoC concentrations above baseline for ten BLM parcels.

Summary Statistic	As	Cd	Cu	Pb	Zn
Minimum	1.4	0.5	6.7	2.0	3.5
Maximum	17.1	11.4	102.4	17.5	83.9
Mean	6.2	3.2	35.0	5.8	17.9

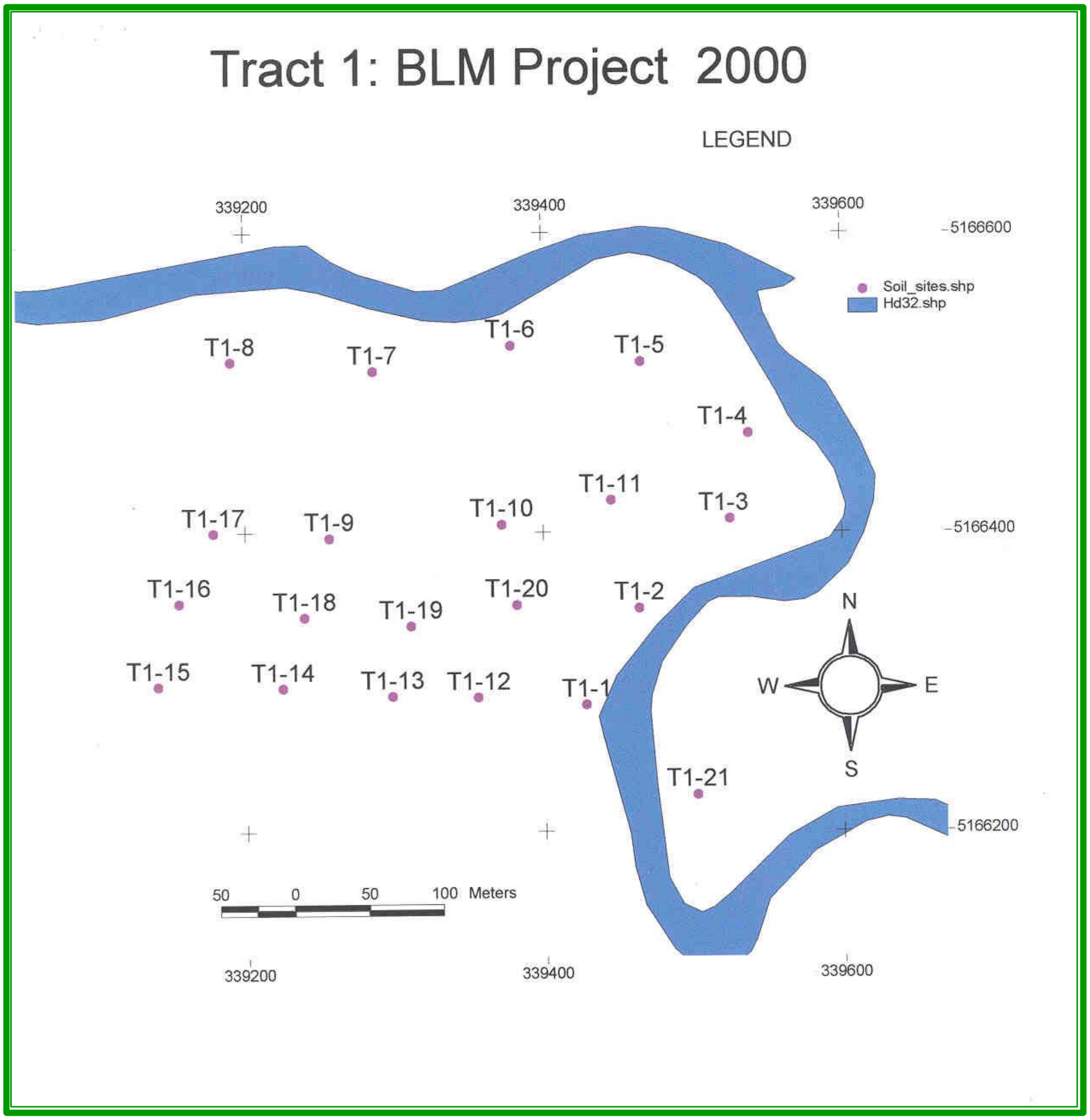

Figure 8. Layout of sampling locations for BLM Tract 01.

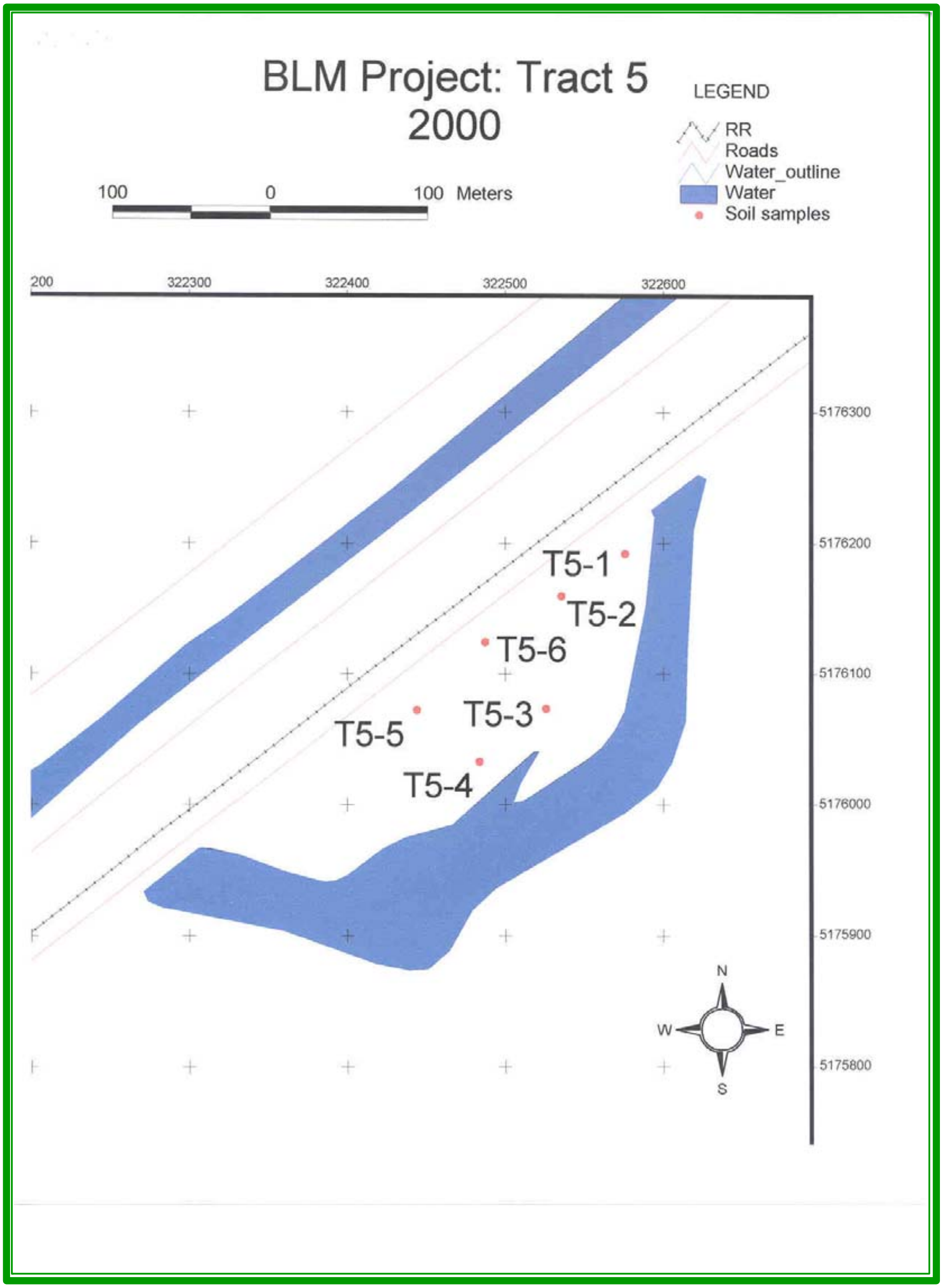

Figure 9. Layout of sampling locations for BLM Tract 05.

Table 3. CoC values for the ten BLM tracts sampled in 2000 and 2001

Tract	Summary Statistic	pH	As	Cd	Cu	Pb	Zn
T01	Minimum	7.00	14	1.0	107	34	187
	Maximum	7.92	171	11.4	1,299	173	4,113
	Median	7.46	60	3.8	532	74	757
	Mean	7.47	74	4.5	609	89	1,256
	Standard Deviation	0.24	43	3.2	384	43	1,096
T03	Minimum	7.11	29	1.6	210	50	450
	Maximum	8.19	84	4.2	1,100	230	1,100
	Median	7.93	49	2.4	395	76	695
	Mean	7.85	52	2.7	439	89	738
	Standard Deviation	0.27	16	0.9	237	47	202
T04	Minimum	7.31	19	1.4	359	107	215
	Maximum	8.14	115	2.6	1,054	218	460
	Median	7.77	39	1.7	447	139	237
	Mean	7.73	49	1.8	529	147	275
	Standard Deviation	0.29	34	0.4	264	38	93
T05	Minimum	7.08	50	1.8	448	95	241
	Maximum	8.06	158	3.9	1,638	298	652
	Median	7.53	128	3.0	1,367	204	579
	Mean	7.56	115	3.0	1,256	206	521
	Standard Deviation	0.36	40	0.8	433	77	149
T07	Minimum	7.90	42	2.7	400	73	770
	Maximum	8.19	67	4.0	550	92	1,100
	Median	8.05	55	3.4	475	83	935
	Mean	8.05	55	3.4	475	83	935
	Standard Deviation	0.21	18	0.9	106	13	233
T08	Minimum	7.11	22	1.9	170	42	640
	Maximum	7.74	37	2.8	310	87	950
	Median	7.66	33	2.3	240	54	830
	Mean	7.50	31	2.3	240	61	807
	Standard Deviation	0.34	8	0.5	70	23	156
T09	Minimum	7.58	68	3.4	550	96	810
	Maximum	8.30	95	4.9	960	120	1,500
	Median	7.95	81	4.3	780	120	1,300
	Mean	7.93	79	4.3	782	111	1,192
	Standard Deviation	0.26	11	0.6	156	12	298
T12	Minimum	7.59	22	0.5	190	45	170
	Maximum	8.05	68	4.8	580	110	1,900
	Median	7.87	44	2.3	370	65	770
	Mean	7.85	42	2.4	340	65	824
	Standard Deviation	0.13	16	1.3	125	20	530
T13	Minimum	7.39	24	1.5	200	43	480
	Maximum	7.89	50	2.9	380	80	770
	Median	7.76	32	2.2	280	58	645
	Mean	7.70	35	2.2	285	60	635
	Standard Deviation	0.22	12	0.6	78	16	124
T15	Minimum	6.86	25	1.3	200	42	430
	Maximum	7.73	50	3.0	480	81	770
	Median	7.74	38	2.2	340	62	600
	Mean	7.30	38	2.2	340	62	600
	Standard Deviation	0.62	18	1.2	198	28	240

2.4.1 Extrapolation of Phytotoxicity

The equations developed from laboratory phytotoxicity test results from GRKO were used to project phytotoxicity response based on pH-adjusted CoC levels (As, Cu, and Zn). According to this method, some level of phytotoxicity is expected at each of the BLM parcels, with maximum phytotoxic effects (i.e., minimum plant growth) ranging from 3% to 28% phytotoxic impact to plant growth.

Table 4. Projected phytotoxicity of BLM tracts based on CoC concentrations and equations derived from GRKO phytotoxicity test results.

Tract	alder			alfalfa			Phytotoxicity Rank			
	mean	minimum	maximum	Mean	minimum	maximum	N	P0	P1	P2
T01	90%	79%	100%	86%	72%	100%	21	7	13	1
T03	95%	84%	100%	94%	79%	100%	12	11	1	0
T04	96%	93%	100%	94%	90%	100%	6	6	0	0
T05	90%	81%	95%	86%	75%	93%	6	3	2	1
T07	94%	91%	96%	91%	88%	95%	2	1	1	0
T08	99%	97%	100%	98%	96%	100%	3	3	0	0
T09	93%	91%	93%	90%	87%	91%	5	4	1	0
T12	94%	87%	100%	92%	83%	99%	9	7	2	0
T13	93%	91%	95%	90%	87%	93%	4	3	1	0
T15	94%	90%	98%	92%	86%	98%	2	1	1	0
						Totals	70	46	22	2

N = number of samples; P0 = non-phytotoxic; P1 = mildly phytotoxic; P2 = moderately phytotoxic

2.5 Conclusions

Hazardous substances from large-scale mining operations upstream of the BLM have contaminated the soils of these parcels. Contamination, like that upstream, is patchy and generally confined to the floodplain. The geochemical processes described for the upstream areas on the GRKO operate on the BLM soils, though the magnitude of contamination is less severe. Nevertheless, continuing releases of hazardous substances are occurring as CoC are mobilized by groundwater percolating and wicking through the soils. Erosion of streambanks also provides a continual source of newly exposed tailings.

The levels of contamination are significantly above background concentrations. At the higher concentrations, the levels are sufficiently high to cause phytotoxic responses in the species tested. These effects diminish the capacity of the lands to supply the expected services of the localized areas of contamination in the floodplain. Natural resource injuries include:

1. Alteration in the vegetative composition of the affected areas of the riparian corridor;
2. Loss of land due to tailings-related stream bank instability;
3. Reduced productivity in the affected areas;
4. Potential for increased ecological vulnerability to drought, fire, disease, and infestation in the affected areas;

5. Reduction in grazing area available for livestock;
6. Degradation of terrestrial wildlife habitat; and
7. Increased operational costs for management.

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